SIMULATION OF CARBON DIOXIDE - MONOETHANOLAMINE - WATER SYSTEM USING EQUILIBRIUM APPROACH

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CERTIFICATE

This is to certify that the thesis entitled, "**SIMULATION OF CARBON DIOXIDE - MONOETHANOLAMINE - WATER SYSTEM USING EQUILIBRIUM APPROACH**", submitted by Mr. Devesh Prasad Mishra , Roll No. 110CH0393 in partial fulfillment of the requirements for the award of degree of Bachelor of Technology in Chemical Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the report has not been submitted to any other University / Institute for the award of any Degree or Diploma

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ABSTRACT

Carbon Dioxide is a greenhouse gas and has been identified as the prime source of global warming and climate changes. So the major challenge ahead of us is the capture and removal of CO_2. Though there are different methods and technologies available, the most efficient method is the use of an absorption/stripping process with a chemical solvent for absorption. Various solvent have been tried, but aqueous monoethanolamine remains the most common and popular solvent.

This thesis focuses on the development of a comprehensive flowsheet based on the thermodynamic model which assumes the overall process to be at equilibrium. The ASPEN PLUS software was used for developing and simulating the problem. The Electrolyte–NRTL model was chosen as the base method with ensured the use of predefined physical properties, thermodynamics and kinetics for the simulation of the process. Once the simulation is over and it properly converges giving an acceptable capture percentage , sensitivity analysis were carried out to study and get an rough idea about the nature and extent of the effect of different parameters on the reboiler duty or energy requirement and other properties like amine flow rate . The simulation based on thermodynamic model is the stepping stone for the more complex and tedious rate based studies as its gives us an estimate of different properties and constraints.

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NOMENCLATURE

G^{ex*}……..	Molar excess Gibbs free energy
$G^{ex*, LR}$…….	Long-range contribution to molar excess Gibbs free energy
$G^{ex*, local}$……	Local interaction contribution to molar excess Gibbs free energy
G^{E}……..	Excess Gibbs free energy
G^{id} ……...	Excess Gibbs free energy if the mixture were ideal
H^{E}……...	Excess Enthalpy
S^{E}……	Excess Entropy
K_j ……...	Equilibrium constant
A_i ……...	Activity of component i in the solution
¥……..	Stoichiometric coefficient of component i in reaction j.
H_{CO2} ……...	Henry's constant of CO_2 in the solvent
P_{H2O}^{*}……	Vapor pressure of Hydrogen
P_{MEA}^{*}……	Vapor pressure of MEA
L ……	Total liquid flow
G ……	Total vapor flow
KJ…….	Kilojoule
Kg……....	Kilogram

CHAPTER-1

INTRODUCTION

1.1 NEED FOR ABSORPTION OF CO_2

CO_2 is a greenhouse gas which contributes significantly to the increasing global temperatures. The concentration of the atmospheric CO_2 is increasing steadily and has risen 35% since the Industrial Revolution. This rate, at which the concentration of CO_2 is increasing, it is unlikely to slow down if no steps are taken in this regard [1]. The Assessment Report of the Intergovernmental Panel on Climate Change (IPCC) estimated CO_2 concentration to contribute to a global radiative forcing of 1.66 Wm-2, which is the greatest of all of the earth radiative components [2]. The largest sources of this emission are fossil fueled power plants especially those plants which use coal as their primary fuel. Because of the role of CO_2 in global warming, its absorption and mitigation are of prime importance. Moreover CO_2 removal is important and practiced in many industries since a long time. CO_2 is removed from natural gas to reduce cost of transportation and compression whereas it is needed to remove carbon dioxide from hydrogen during Ammonia generation to prevent poisoning of the catalyst. Chemical absorption using amines have been widely used for CO_2 removal. But the large flow rates of the flue gases with huge amount of CO_2 in it, pose a serious challenge to such processes.

1.2 OVERVIEW OF CO_2 CAPTURE SYSTEM

The CO_2 capture system used in power plants can be broadly divided into 3 categories:-

- Post Combustion Capture
- Oxyfuel Combustion
- Pre Combustion Capture

1.2.1 Post-Combustion Capture

In post-combustion capture, CO_2 is removed, once the combustion of fuel has taken place, from the resultant flue gas. A schematic of the post-combustion capture is shown in figure 1-1.

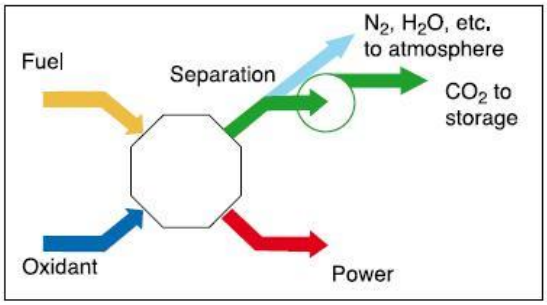

Figure 1-1: Schematic of post-combustion capture ([2])

A capture and compression system is necessary in this method. These technologies also require that the flue gas must be cleaned properly before they are fed into the capture device. The particulate matter and sulfur dioxide matter need to be removed as they result in fouling and corrosion. There are a number of methods that can be used for the post-combustion capture of CO_2 from flue gases. These include:

- Chemical absorption
- Physical absorptions
- Membrane separation
- Adsorption
- Cryogenic separation

Different methods have been proposed for removing CO_2 from flue gases on a large scale. The main techniques that can be used for the separation of CO_2 from other light gases are: cryogenic distillation, membrane separation, absorption using liquids, and adsorption using solids. Cryogenic distillation is generally not used for separation of CO_2 from flue gases because of the high energy cost. Membranes can be used very efficiently for separation especially when the components passing through the membrane are present in a large concentration [3].

To separate the acid gases from gaseous stream usually absorption technique is used with the help of a liquid media. The liquid media are generally aqueous alkanolamines solutions or other solutions with alkaline character, such as chilled or ambient temperature ammonia. The chemical reactions which take place between the acidic gases and the aqueous absorbent facilitate the absorption.

1.2.1.1 Chemical absorption

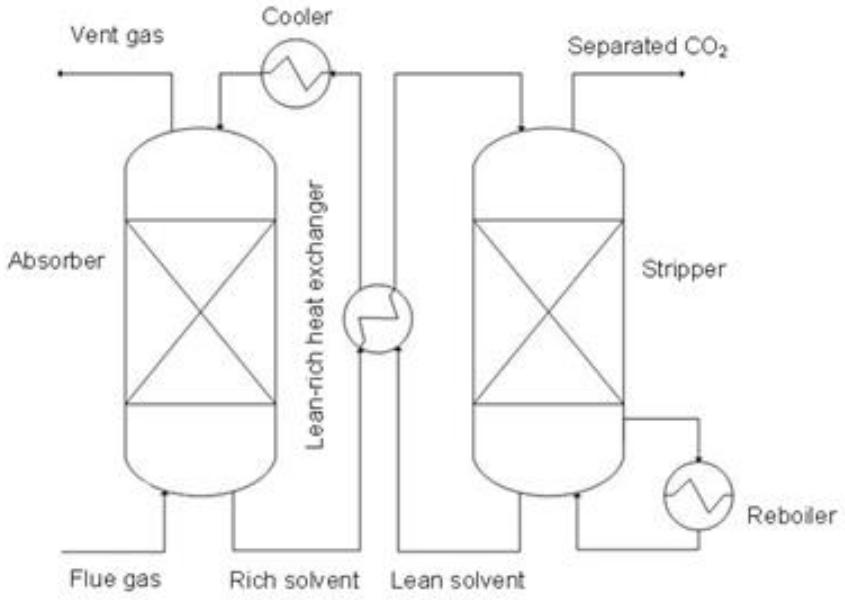

Figure. 1-2 Schematic of CO_2 capture by chemical absorption

Chemical absorption at present is the most preferred option for post-combustion capture of CO_2. The liquid media can be aqueous alkanolamines, (MEA being the most widely known solution) or other solutions such as chilled liquid ammonia and K_2CO_3 solution [4] .This mainly consist of an absorber and a desorber or stripper column. In the absorber, a reversible chemical reaction takes place between CO_2 and an aqueous alkaline solvent. This helps in the absorption process. In the desorber, with the help of a reboiler, stripping of the absorbed CO_2 from the rich liquid stream takes place. The gas obtained is sent for storage after compressing it to the desired pressure while the lean stream is recirculated back to the absorber.

Reboilers provide the necessary heat to generate steam which will ultimately carry off the CO_2 with it. In addition, energy is also required for compression and storage of CO_2 as well as for the working of pumps and blowers. There are actually three main classifications of alkanolamines: primary, secondary, and tertiary amines. Among these three categories the primary amines, such as MEA, are considered the most efficient and convenient for flue gas cleaning due to the low partial pressure of CO_2 in the flue gas. MEA is more popular and useful

solvent at low partial pressures of CO_2 because it reacts at a rapid rate and the cost of the raw material is low compared to other similar amines.

1.2.2 Oxyfuel Combustion

The main disadvantage of the previous system is the dilution of the flue gases because of nitrogen. This problem can be tackled if the combustion is carried out with oxygen directly. The burning of fossil fuel in an atmosphere of oxygen leads to very high temperatures (3500°C). The temperature has to be controlled and maintained at a level such that the material of construction can withstand such high temperature. Figure 1-3 depicts Oxyfuel combustion.

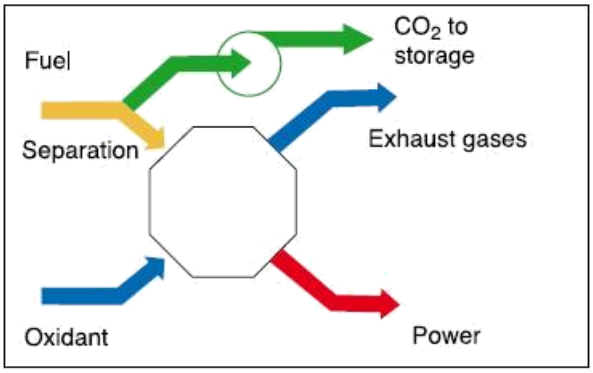

Figure 1-3: Schematic of Oxyfuel combustion ([2])

In oxy-fuel combustion fossil fuels are burnt in a mixture of oxygen (95% purity or higher) and flue gas. Combustion temperature is generally controlled by recycling CO_2 rich exhaust gas. From the other part which is rich in carbon dioxide and water, water vapor are condensed off and CO_2 is separated after cleaning the gas which is then compressed and transported to storage or other suitable applications. This method enables 97 % CO_2 capture along with very low NOx emissions. [5]

1.2.3 Precombustion Capture

In precombustion capture, before combustion starts, the carbon content of the fuel is reduced so as to obtain a stream of pure CO_2 upon combustion. Precombustion technique can be used to produce hydrogen or generate electricity or both. Figure 1-4 shows precombustion capture method.

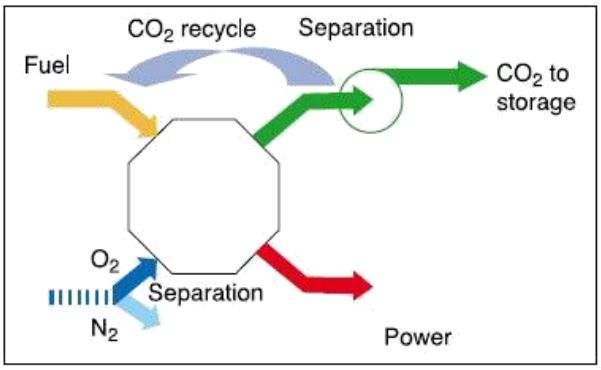

Figure 1-4: Schematic of precombustion decarbonization ([2])

The fuel bound carbon is initially reacted with a mixture of oxygen and steam. Carbon monoxide and hydrogen are mainly produced which is called as synthesis gas or syngas. Two additional processing units are required to capture CO_2 from syngas. Carbon monoxide is converted to CO_2 in shift reactor and separated out from the hydrogen. The CO_2 thus obtained is compressed and then stored and Hydrogen rich gas is used for power generation.

The different flue gas sources and CO_2 concentration in them is given below

Table 1-1: CO_2 partial pressure in flue gases of different combustion systems. ([2])

Flue gas source	CO_2 concentration, % (dry)	Pressure of gas stream, MPa	CO_2 partial pressure, MPa
Natural gas fired Boilers	7-10	0.1	0.007-0.01
Gas turbines	3-4	0.1	0.003-0.004
Oil fired boilers	11-13	0.1	0.011-0.013
Coal fired boilers	12-14	0.1	0.012-0.014
IGCC after Combustion	12-14	0.1	0.012-0.014
IGCC synthesis gas after gasification	8-20	2-7	0.16-1.4 (before shift)

1.3 OBJECTIVE OF THE THESIS

The objective of the thesis is to develop an energy efficient absorption and capture system for CO_2 using monoethanolamine solvent.

1.4 SCOPE OF THE THESIS

The scopes of the thesis are as follows:-

- To develop a consistent flowsheet representing the actual CO_2 capture and storage technique using MEA as the solvent. The flowsheet must represent the complete process in detail taking care of all process equipment.

- To successfully model the flowsheet using Thermodynamic Model and by using E-NRTL base method which represents all the properties and other parameters.

- To complete the flowsheet by providing realistic input data, chemical reactions and important design specifications required for convergence and good performance.

- To study the effect of loading, capture percentage, temperature approach and other similar parameters on reboiler duty and to find important information about operational limit and other working constraints.

1.5 OUTLINE OF THE THESIS

Chapter 1 of thesis talks about the need for absorption and capture of CO_2. It also gives us insight into the different capture system available and used in industries. In chapter 2 the different solvents that are used for CO_2 capture are described. It also describes the reaction mechanism of alkanolamines with carbon dioxide and the different methodologies applied for CO_2-MEA-H_2O system. In chapter 3 the process of CO_2 capture by MEA is explained along with the reactions and thermochemistry. In chapter 4 the Thermodynamic Model used in this thesis is described in detail along with basic information about the rate model. The chapter 5 of

this work is about the simulation of the process using thermodynamic model. Here different input and design specifications are mentioned. Chapter – 6 deals with the results obtained from the simulation and give an inference about the results. The Chapter-7 represents the conclusion and the future work that can be carried out later.

CHAPTER-2

LITERATURE REVIEW

2.1 SOLVENTS USED FOR CO_2 CAPTURE

CO_2 capture is basically done by absorption with aqueous alkanolamines. These amines are bases which react with acid species. The alcohol groups enable them to be soluble in water. The first alkanolamines to be used industrially was Monoethanolamine (MEA). They may categorized into primary , secondary , tertiary types according to the number of organic groups that are attached to the alkaline nitrogen .These varieties of amines have different reaction mechanism , reaction products and the heat of reaction. Primary and secondary amines usually react faster than tertiary amines with higher heat of absorption in these amines. While the advantage of fast reacting amine solvent is a smaller absorber, the main difficulty is the energy required to regenerate the solvent. As a result a proper solvent must be selected. Several works are being carried out to develop mixed solvents so as to make this procedure more effective. Bishnoi (2000) [6] and Dang (2001)[7] have been working in this regard by working on Piperzine promoted MDEA and MEA respectively. Cullinane (2002) also studied the use and properties of Piperzine promoted potassium carbonate. But still more work is required and thus these mixed solvents are not yet used in industry. [8]

2.2 ALKANOLAMINE AND ITS REACTION WITH CO_2

In CO_2 absorption, carbamate formation is a very important step.. Two mechanisms have been proposed for the formation of the carbamate **– the zwitterion mechanism and the termolecular mechanism**

2.1.1 Zwitterion Mechanism

This mechanism was proposed by Caplow in 1968 [9].

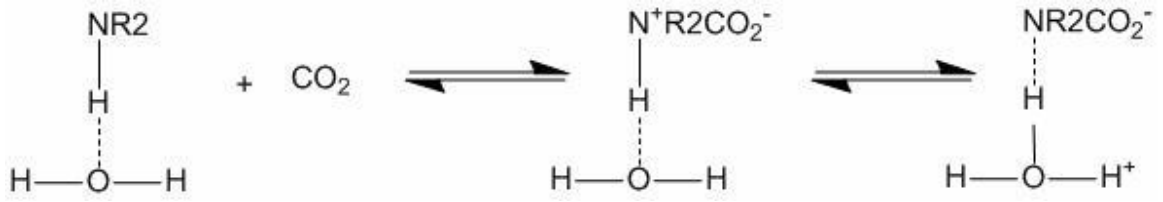

Figure 2-1: Zwitterion mechanism for carbamate formation [9]

According to Caplow hydrogen bond is formed between the amine and the water molecules before any reaction with CO_2 takes place. Initially an unstable intermediate was formed due the bonding between the amine and the carbon dioxide molecules. Next a carbamate is formed by the transfer of the amine proton. The base used basically is either water molecule or an amine. The kinetic expressions for this , was given by Kumar *et al*. in 2003. In lean aqueous solutions, the deprotonation of the zwitterion is caused by OH^- to form the carbamate species.

2.1.2 Termolecular Mechanism

A termolecular single-step mechanism for carbamate formation was proposed in 1989 [10]] and is shown in Figure2.2.

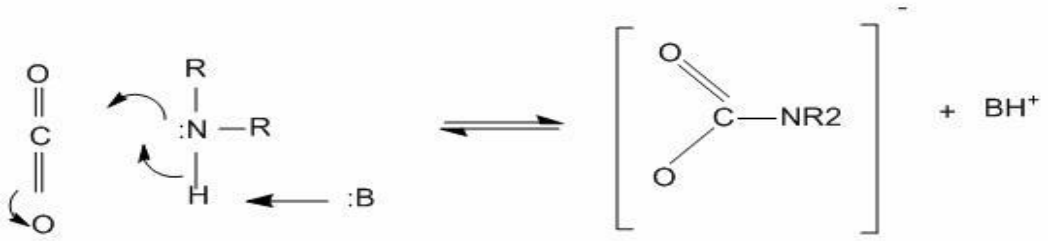

Figure 2-2- Termolecular mechanism for carbamate formation [10]

In this mechanism, the bond formation between alkanolamines and CO_2 and the proton transfer take place simultaneously. This mechanism described here is actually not very different from the one given by Caplow. Caplow's mechanism approaches the termolecular mechanism when the lifetime of the Zwitterion is very small. Both these mechanism can be fitted to experimental data as they allow and work for different amine concentration. An equally effective representation of reaction rates should be possible using either mechanism.

2.3 MODELING OF CO_2 -MEA-WATER SYSTEM

Over the years large experimental data have been collected on CO2-MEA-H_2O system. These data have been used to study thermodynamic equilibrium, rates of absorption and rates of reaction. To reproduce and validate these data many thermodynamic models and rate models have been created. Among the thermodynamic models, the Kent and Eisenberg Method (1976) were initially best known for its simplicity. Gradually other models were developed and currently the most used model is the Electrolyte-NRTL model, developed by Chen et al. (1979). It is a model

based on excess Gibbs's energy of a mixture and was successfully used over a wide range of temperature and loadings. Rigorous thermodynamic models generally are based on experimental data collected by Joe et al (1995)[11] whereas as Rate models are developed using absorption rate collected by Dang (2001) . This type of modelling is generally done by the help of ASPEN PLUS software. In the past, other models have also been completed using either commercial software or language codes. TSWEET, an amine gas sweetening computer program, have been used since early eighties for modelling of Acid Gas removal and the results are found in the literature (Holmes et al. 1984).[12] Another software that is used is AMSIM, which uses a rigorous non – equilibrium stage model (Zhang et al. 1996)[13]. Also different programs have also been written in FORTRAN or Visual Basic and are specific for amine gas treating. All these different integrated models though provide better insight on the overall phenomena but are usually slower and cause great difficulty in simulating the whole process. ASPEN PLUS on the other hand provides tools to perform analysis of the whole process and understanding the effect of design variable on each other.

CHAPTER-3

MONOETHANOLAMINE SYSTEM

Monoethanolamine (MEA) is widely used for the removal of CO_2 from flue gas and has been described in detail in many sources. For non-selective removal of acid gas, MEA has been extensively used as a solvent for the past 60 years. Presently, attempts are being made by Fluor to commercialize CO_2 capture technologies based on MEA [14]. The Fluor process uses a 30 wt. % MEA solvent. In order to prevent equipment corrosion and solvent degradation the solvent is mixed with inhibitors. In general, if CO_2 is the only acidic gas being absorbed then one can use amine concentration of up to 35 wt. % along with a corrosion inhibitor [15].

3.1 DESCRIPTION OF PROCESS

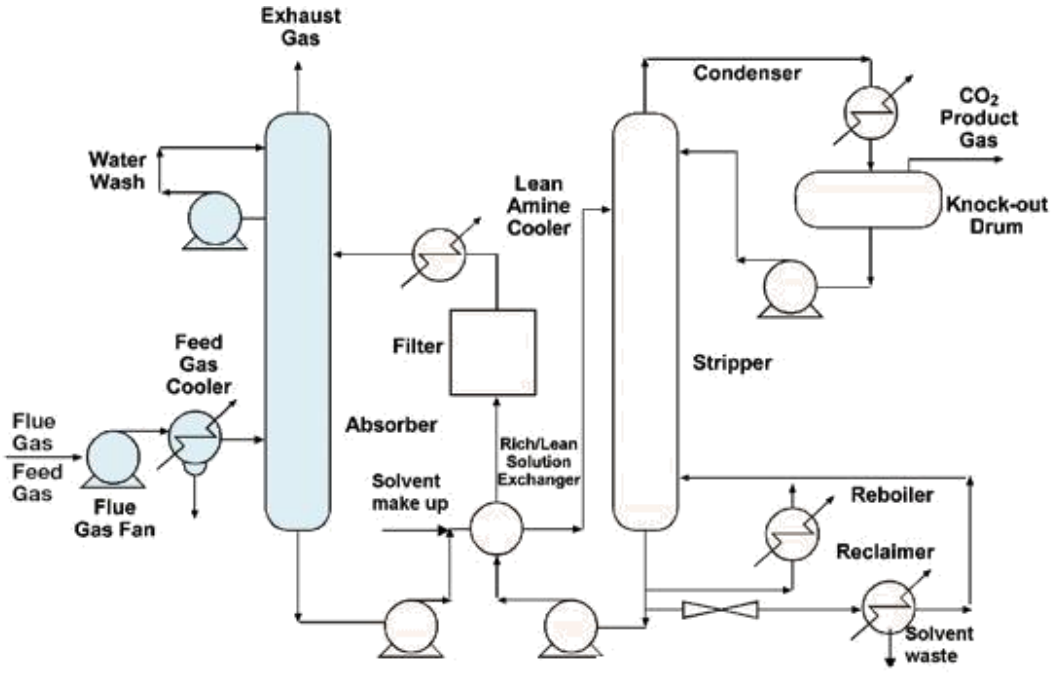

Figure 3-1: Schematic of CO_2 capture by use of MEA solvent ([16]

CO_2 capture using MEA is a combination of absorption and desorption and the whole process can be divided into:-

1. Flue gas cooling and compression
2. Absorption of CO_2 and regeneration of solvent
3. CO_2 compression

A schematic of the process is shown in Figure 3-1 [16]. Each of these steps is discussed in detail below.

3.1.1 Flue Gas Cooling And Compression:

The flue gas coming out as exhaust in the power plants are generally at a temperature of 110-120^{o}C. But the absorber used in this process works at temperature of 40^{o}C and hence the inlet to the absorber must be around 40-50°C. For this reason the flue gas must be initially cooled before being fed into the absorption column.

The flue gas is cooled with the help of a direct contact cooling tower (DCC). The DCC is a packed tower with provisions for counter-current flow of cooling water and the flue gases. The cooling water enters from the top whereas the flue gas is fed from bottom. In the tower, cooling of flue gas is achieved by evaporation of water and as a result, the water content of the flue gas gets ultimately reduced at the exit of the tower. The cooling water is recycled back from the bottom to reduce its temperature so that it can again be used in the DCC.

The flue gas is then sent to a blower from the top of the DCC for compressing it slightly. The pressure of the flue gas has to be increased before entering a absorber as it has to flow upward through a packed tower .This is also accompanied by slight temperature increase. NO_x and SO_x tend to react irreversibly with MEA to form heat stable salts . These lead to loss of solvent and it cannot be reclaimed from the salts. Hence these components are undesirable and steps must be taken to reduce their concentration. NO_2 is mainly responsible for such kind of irreversible reaction. A NO_2 level of less than 20 ppmv is desired. For MEA, a SO_x level of less than 10 ppmv is recommended for the Fluor Daniel Econamine^{TM} process [17].

3.1.2 Absorption Of CO_2 And Regeneration Of Solvent:

The absorber is basically a packed column, which provides enough surface area for effective absorption of CO_2. The flue gas enters at the bottom of the absorber and the lean amine solvent enters at the top of the absorber. The loading of the inlet lean amine is around 0.2-0.3 and its leaves with CO_2 as rich amine with a loading of 0.5. In a MEA system, the loading is defined on a mole basis as:-

$$\text{Loading} = \frac{\text{Moles of all } CO_2}{\text{Moles of all MEA}} \qquad \textbf{(3-1)}$$

$$\text{Loading} = \frac{[CO_2] + [HCO_3^-] + [CO_3^{2-}] + [MEACOO^-]}{[MEA] + [MEA^+] + [MEACOO^-]} \qquad \textbf{(3-2)}$$

Make-up water is fed at the first stage. Any entrained MEA that may be carried out through the vent can be removed as this make-up water act as water wash. The amine stream is introduced on the second stage from the top. The make-up water also serves the purpose of cooling the vent gas before releasing it into the atmosphere. From the bottom of the absorber the rich amine is sent to cross heat exchanger after passing it through a pump.

After exchanging heat with the lean amine the rich stream is sent to the desorber. The desorber is a packed column along with a kettle reboiler for providing the necessary heat for stripping. The desorber usually operates at slightly elevated pressures (~1.5-1.8 atm). In the desorber , the stripping of CO_2 takes between the rich amine and vapors or steam produced by the reboiler .These vapors carry the CO_2 out from the top the desorption column where it is first cooled and the fed into a flash drum for separating the CO_2 and water. A part of this water is recycled back to column and excess water is removed by a splitter as excess stream. The CO_2 is sent for compression and storage.

3.1.3 CO_2 Compression:

The CO_2 gas obtained from the flash drum needs to be dried and compressed before it is fit for storage. During the transport of CO_2 gas any kind moisture presence can lead to corrosion of pipelines and equipment. As a result drying becomes very important. Drying and compression, both can achieve by the use of a 4-stage reciprocating compressor with provision of cooling between the stages. This not only helps in separating out the water present but also compresses the CO_2 to 90 atm. The CO_2 is further compressed to 130 atm with the help of pumps so that these can be easily stored and transported as supercritical liquid.

3.2 CHEMISTRY OF THE MEA SYSTEM

In the MEA system, CO_2 is solubilized in the liquid phase either in a carbamate, carbonate or bicarbonate form. The following reversible reactions occur in the MEA system:

$$2\ H_2O \leftrightarrow H_3O^+ + OH^- \qquad \textbf{(3-3)}$$

$$CO_2 + 2\ H_2O \leftrightarrow HCO_3^- + H_3O^+ \qquad \textbf{(3-4)}$$

$$MEA + HCO_3^- \leftrightarrow MEACOO^- + H_2O \qquad \textbf{(3-5)}$$

$$MEA + H_3O^+ \leftrightarrow MEA^+ + H_2O \qquad \textbf{(3-6)}$$

$$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+ \qquad \textbf{(3-7)}$$

The equilibrium constants for the reaction are temperature dependent and follow the dependence given in (3-8).

$$\ln K_x = A + \frac{B}{T} + C \ln T + DT \qquad \textbf{(3-8)}$$

In this case, T is the temperature in °K. The constants A, B, C, D for the different reactions are presented in Table 3-1 and are referenced from Augsten's work [18].

Table 3-1: Values of temperature dependent parameters for equilibrium constant in MEA system

Reaction	A	B	C	D
(3-3)	132.89	-13445.9	-22.47	0
(3-4)	231.46	-12092.1	-36.78	0
(3-5) (reverse)	-0.52	-2545.53	0	0
(3-6)(reverse)	-3.038	-7008.3	0	-0.00313
(3-7)	216.05	-12431.7	-35.48	0

3.3 THERMOCHEMISTRY IN THE MEA SYSTEM

The thermochemistry of the MEA system has been established by Rochelle et al. [19]. The values as presented in Rochelle et al. [20] are presented below:

Table 3-2: Thermochemistry in the MEA system.

Reaction	- H (kcal/mol)		
	25°C	80°C	120°C
CO_2 (g) → CO_2 (aq.)	4.9	2.9	1.3
CO_2 (*aq*) + H_2O → HCO_3^- + H^+	-2.2	1.7	4.7
MEA(aq) + H^+ → MEA^+	12.0	12.2	12.1
MEA (aq) + HCO_3^- → $MEACOO^-$ + H_2O	4.3	5.1	5.4
Overall reaction	18.9	21.9	23.6

CHAPTER-4

THERMODYNAMIC AND RATE MODEL

There are actually 2 types of modelling which are used for simulation and analysis of CO_2-MEA-H_2O system. These are

- Thermodynamic Modeling
- Rate Based Modeling

4.1 THERMODYNAMIC MODEL

Thermodynamic model assumes the overall process to be at equilibrium although CO_2 absorption is a non-equilibrium process. The vapor and the liquid are assumed to be at equilibrium at each stage of the column. In this model the absorption/stripping process require rigorous thermodynamics. To determine the amount of conversion that can take place or for convergence of the simulation we need to have knowledge about their equilibrium compositions. When MEA is used for CO_2 absorption process, it is observed that ions and polar molecules are formed and as a result of which Electrolyte-NRTL framework is generally used to describe the thermodynamic model..

4.1.1 Electrolyte NRTL Model

Chen and Evans (1979) originally developed the model which was later extended by Mock Et .al for various other mixed solvents. The Electrolyte – NRTL model is based on the excess Gibbs free energy of a solution. This model considers the presence of polar ions and states that the excess Gibbs free energy in the electrolyte system is the sum of two contributions [20-21]:

1. Short-range forces between all the species that includes the local ion-molecule, ion-ion, and molecule-molecule interactions.
2. Long-range electrostatic ion-ion interactions.

Thus, the expression for the excess Gibbs free energy as calculated by the Electrolyte NRTL model can be expressed as:

$$G^{ex*} = G^{ex*,\,LR} + G^{ex*,\,local} \qquad \textbf{(4.1)}$$

G^E is the excess Gibbs free energy, defined as

$$G^E=G-G^{id} \quad \textbf{(4.2)}$$

Where G^{id} is the excess Gibbs free energy if the mixture were ideal. The excess Gibbs free energy is related to excess enthalpy and excess entropy of mixing by

$$G^E=H^E-TS^E \quad \textbf{(4.3)}$$

In process involving MEA, ions are present in large numbers which tend to interact which each other strongly. The CO_2 molecules present tend to reduce these interactions. Moreover as the composition changes the interactions between the different component also changes and the excess enthalpy is determined from it. It is also observed because of these reasons the CO_2 tend to leave the liquid phase when the solution has high ionic strength, because this results in reducing the overall enthalpy. With the help of the theory of Debye-Huckel which was later modified by Pitzer the long term ionic forces can be described. The ionic strength of solution affects these forces to a great extent. .The molecular forces which are basically short range forces, need to be included in the model to include the effect of hydrogen bonds and local interactions of molecules with molecules, molecules with ion pairs and ion with ion pairs. Thus the E-NRTL model is mainly based on 2 assumptions

- **Like-ion repulsion assumption:** It is assumed the local composition of cations and anions around themselves is zero due to the large repulsive forces present between the same ionic charged particles..
- **Local electro neutrality assumption:** It is also assumed that the distribution of the cations and anions around a central solvent molecule is there in such a manner that ensures the net local ionic charge to be zero.

4.1.2 Solution Chemistry And Equilibrium Governing Equations

The following reversible reactions occur in the liquid phase when CO_2 is absorbed into an aqueous solution of MEA [22]

$$MEACOO^-+H_2O \leftrightarrow MEA+ HCO_3^- \quad \text{------- } (K=K_{CARB}) \quad \textbf{(4.4)}$$

$$CO_2+2H_2O \leftrightarrow HCO_3^-+H_3O^+ \quad \text{------- } (K=K_{a,CO2}) \quad \textbf{(4.5)}$$

$HCO_3^- + H_2O \leftrightarrow CO_3^- + H_3O^+$ ------- ($K=K_{A,\ HCO3^-}$) **(4.6)**

$MEAH^+ + H_2O \leftrightarrow MEA + H_3O^+$ ------- ($K=K_{A,\ MEAH^+}$) **(4.7)**

$2H_2O \leftrightarrow H_3O^+ + OH^-$ ------- ($K=K_W$) **(4.8)**

For every reaction there exists an equilibrium constraint. We need to find the mole fraction of each component in both the phases to ultimately solve the thermodynamic problem for a CO_2-MEA-H_2O system. These data are to be found at a particular temperature and pressure. Since the ions present are non-volatile, only H_2O, MEA, CO_2 are in vapor phase. So we face a situation where there are 9 components, and 12 unknowns with 12 equations. The MEA concentration and loading of CO_2 in the solution are the known variables in the problem. The solving equations are the equations for the five equilibrium constraints(equation-4.9), the CO_2 material balance(equation 4.10), the MEA balance(equation 4.11), the total material balance(equation 4.12), electro neutrality(equation 4.13) and the phase relationships for CO_2,MEA and water balance(equation 4.14-4.16) [22]

$$K_j = \pi_i(a_i)\text{reactant} / \pi_i(a_i)\text{product} \quad \textbf{(4.9)}$$

$$X_{CO2\ total} = X_{CO2} + X_{HCO3^-} + X_{CO3^-} + X_{MEACOO^-} \quad \textbf{(4.10)}$$

$$X_{MEA\ tot} = X_{MEA} + X_{MEAH^+} + X_{MEACOO^-} \quad \textbf{(4.11)}$$

$$1 = x_{CO2} + x_{MEA} + x_{H20} + x_{HCO3^-} + x_{CO3^-} + x_{MEACOO^-} + x_{MEAH^-} + x_{H3O^+} + x_{OH^-} \quad \textbf{(4.12)}$$

$$0 = (x_{HCO3^-} + x_{MEACOO^-} + x_{OH^-} + 2x_{CO3^-}) - (x_{MEAH^+} + x_{H3O^+}) \quad \textbf{(4.13)}$$

$$P_{yCO2} = ¥_{CO2}{}^{*} H_{CO2} X_{CO2} \quad \textbf{(4.14)}$$

$$P_{yH2O} = ¥_{H2O} P_{H2O} X_{H2O} \quad \textbf{(4.15)}$$

$$P_{YMEA} = ¥_{MEA} P_{MEA}{}^{*} X_{MEA} \quad \textbf{(4.16)}$$

A_i=activity of component i in solution and ¥ is the stoichiometric coefficient of component i in reaction j.

H_{CO2}=Henry's constant of CO_2 in the solvent

P_{H2O}^{*} and P_{MEA}^{*}=vapor pressure of H_2O and MEA respectively

But there are some errors or disadvantages of this method. Since the loading changes the MEA concentration as well as the ions present, the reference state assumed initially also should vary. But as the Gibbs free energy of formation is assumed to be fixed these changes cannot be incorporated in the model. This ultimately results in a thermodynamic bug or problem in the ASPEN PLUS.

4.2 RATE MODEL

The absorption of carbon dioxide in monoethanolamine is actually a non-equilibrium process. The CO_2 reacts with MEA at a finite rate and according to specific kinetics. The reaction take place at fast rate but they are not close to equilibrium at the operating conditions. Hence, in these cases, a more robust Rate- Based Model is used.

The RATEFRAC mode in Aspen Plus is used for the rate based simulation of the desorber and the absorber. [23]. It is a stage based model and incorporates mass and heat transfer phenomena as well as the kinetics of chemical reactions. The various equations that are solved in ASPEN RateSep include [23]:

- Mass and heat balances for the vapor and liquid phases
- Mass and heat transfer rate models to determine interphase transfer rates
- Vapor-liquid equilibrium equations for the interphase
- Estimation of mass and heat transfer coefficients and interfacial areas
- Enhancement of mass and heat transfer processes by chemical reactions

The two-film theory is used to explain the process and uses film discretization technique for accurate concentration profile. It also combines the film equations with separate balance equations for the liquid and vapor phase, diffusion and reaction kinetics, electrolyte solution chemistry and thermodynamics [24].

In this work we are focusing only on Thermodynamic modelling. Using the results of thermodynamic modeling one is able to get the desired results and further synthesis the process using the Rate based Model.

CHAPTER-5

SIMULATION ACCORDING TO THERMODYNAMIC MODEL

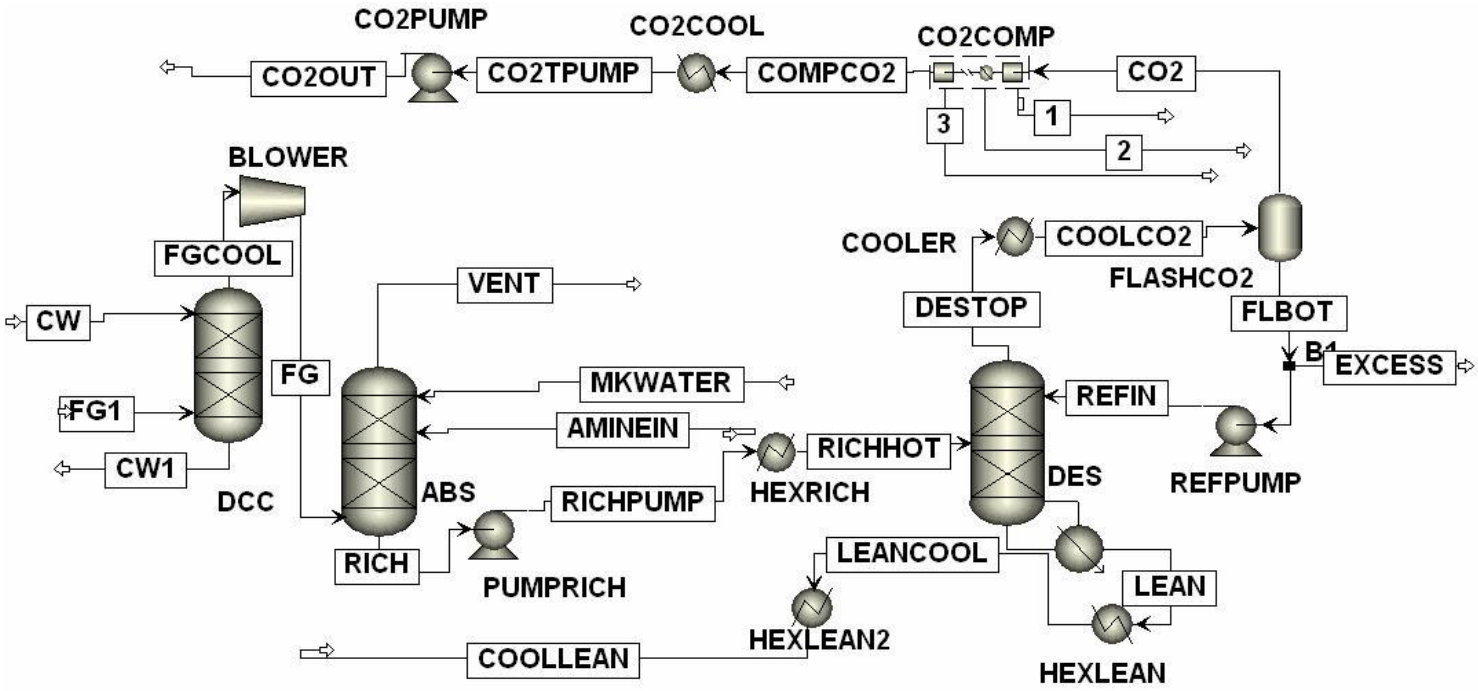

Figure 5-1: Flowsheet of MEA system as developed in ASPEN Plus [25]

The thermodynamic model was applied and thus the absorber and desorber were developed as a set of stages each at equilibrium conditions. The flow sheet was modeled as an open loop system to facilitate easier convergence. This also helped to carry out multiple simulations quickly. But for the open loop system to converge we need some robust design specifications which take care of parameters important for the convergence of the process. The different reactions provided were also assumed to be at equilibrium and data for their equilibrium constant was fed.

The above flowsheet was developed in ASPEN PLUS software. The absorber, desorber and direct contact cooling tower (DCC) were selected and modeled as RADFRAC columns with desorber having a kettle reboiler. [25] The flash is a high pressure separator which separates the CO_2 and

water. A dot splitter was used to remove the excess water and a fraction was recycled back to the desorber. The CO_2 so obtained was sent to the 4 stage reciprocating compressor with cooling in between stages. In each stage a gradual compression takes place and finally CO_2 was obtained at 90 atm pressure. The compressor was a MCOMP model and water was decanted out in each stage. A set of pumps and heaters were selected and used for varying pressure and temperature to the required value.

5.1 STEPS INVOLVED IN DEVELOPING THE FLOWSHEET

- After providing the project title and name of the account, first the different components were selected as shown below.

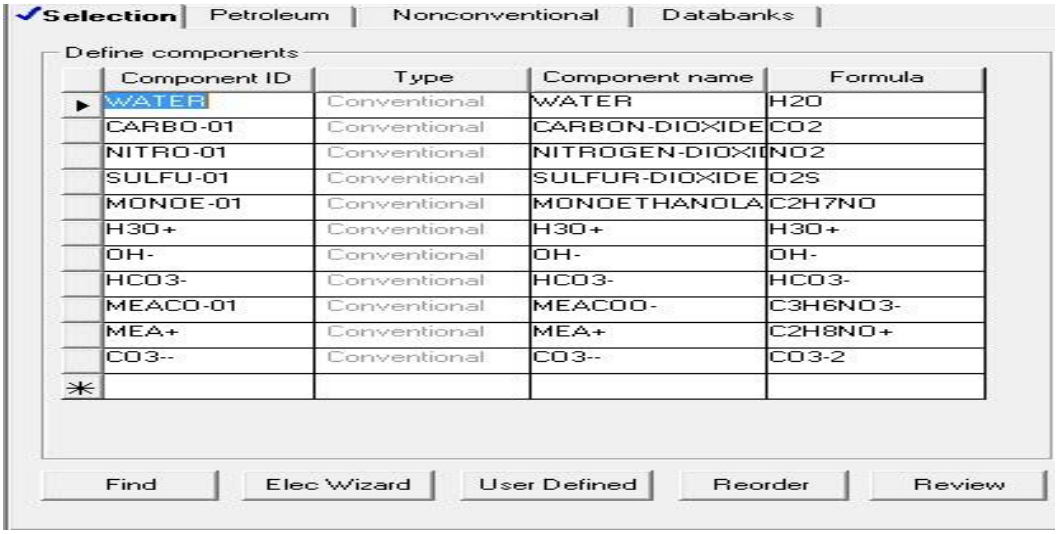

Figure -5-2 Different components selected in ASPEN PLUS

- After selecting the components we set the base method as E-NRTL and all the properties were defined according to it.

- The different input streams were next given. The Flue gas was initially fed to the DCC at a temperature of 115^{o}C and 1 atm pressure along with cooling water at 25^{o}C and pressure of 1 atm containing 10 % CO_2. MEA was then fed at 40^{o}C, pressure of 2 atm and a flow rate of 65 kg/hr with initial CO_2 loading of 0.2 to the absorber for absorption. Make up water was provided to the absorber at a temperature of 35^{o}C and pressure of 2 atm to prevent entrainment of amine stream.

- After the streams were successful specified, the input for different blocks were provided. The input specification for the different pumps and heaters are given in table 5-1 and 5-2 respectively.

Table 5-1: Input Specification of Pumps

PUMPS	DISCHARGE PRESSURE(atm)
PUMPRICH	3
REFPUMP	3.5
CO2PUMP	130

Table 5-2: Input Specification of Heaters

HEATERS	TEMPERATURE(^{O}C)	PRESSURE(atm)
HEXRICH	50	3
HEXLEAN	50	1.1
HEXLEAN2	40	1
COOLER	30	1.5
CO2COOL	35	100

- For the DCC, number stages were fixed at 4 with no condenser and the stage1 pressure was set at 0.9 atm .A reflux ratio of 2 was maintained for the column. For the Absorber, the number stages were fixed at 12 with no condenser or reboiler and the stage1 pressure being 1.5 atm. In the case of the Desorber, 8 stages were taken with a kettle reboiler and the stage1 pressure was set at 1.8 atm. Reboiler duty was taken as 5000 KJ/kg. For the desorber a pumparound was defined. It represented an internal reflux from a hotter stage to a cooler one. In this case the pumparound was given from 8^{th} stage to the 1^{st} stage.
- A blower was also used to increase the pressure of the cool flue gas. It was modeled as an isentropic blower with discharge pressure of 2 atm.
- A 4 stage reciprocating compressor was selected and modeled as isentropic one. The outlet stream was obtained at 90atm and 50^{o}C. From all the other stages water was purged out.
- The required reactions mentioned earlier were given and the temperature dependent constants were provided according to the table 5-3.

Table 5-3: - Reaction Data Used for the Reactions

Reaction	A	B	C	D
(3-3)	132.89	-13445.9	-22.47	0
(3-4)	231.46	-12092.1	-36.78	0
(3-5) (reverse)	-0.52	-2545.53	0	0
(3-6)(reverse)	-3.038	-7008.3	0	-0.00313
(3-7)	216.05	-12431.7	-35.48	0

- After providing all the input information the different design specification were given for optimizing and converging the simulations.

The design specifications in the flowsheet are outlined below [25]:

1. **Regulating the Vent:** Vent is required because all the CO_2 is not absorbed in the absorption column. So whatever left comes out through it. As a result we require a design specification which will regulate the amount of CO_2 that comes through the vent and how much is absorbed in the absorber

   For this, first the mass flow rate of AMINEIN and VENT stream were defined. The mass flow rate of the VENT stream was desired to be 1.2 kg/hr assuming 90 % absorption takes place in the absorber with a tolerance of 0.05. The AMINEIN flow rate was varied from 50-70 kg/hr to achieve this target.

2. **Ensuring the convergence of the open loop flowsheet:** The reboiler duty provides the necessary heat required to produce steam which carries the CO_2 upwards from the rich amine and helps in stripping .Since the flowsheet is an open loop one we need to match the composition of the stream COOLLEAN (output from second heat exchanger after desorber) to that of the stream AMINEIN which will eventually ensure that the simulation would converge in a closed loop manner. By matching the loading of the two

streams this condition is met. We need to first develop 2 prop sets in the property module PS-1 and PS-2 and then define FAPPCO2 and FAPPMEA in Prop sets tab which actually calculate the apparent molar flows of CO_2 and MEA in the stream. The ratio of FAPPCO2 to FAPPMEA gives us the loading of the stream. This loading must be equal the initial loading of the AMINEIN stream so that it can be understood and accepted that the COOLLEAN stream can be recycled back to the absorber and the system will converge. This is achieved by varying the reboiler duty of the desorber.

After the prop sets have been defined, design specification of the desorber was specified. This design specification checks the property ratio or the ratio of the two prop sets of the LEAN stream coming out of the desorber. The reboiler duty was varied from 5000 to 15000 watt to reach the desired loading of 0.2 as of the AMINEIN stream.

3. **Satisfy the conditions for Cross Heat Exchanger:** In this flowsheet, the two separate heat exchangers – HEXRICH and HEXLEAN function as a cross heat exchanger to ensure that a closed loop is not formed. As a result the heat duties of the two heat exchangers will be equal but of the opposite sign. To ensure this a design specification was provided in the Flowsheeting options tab which regulates the heat duties of the exchangers..

   Initially the heat duties of the two heat exchangers were defined. Since we have assumed that the heat duties of HEXRICH and HEXLEAN are equal but of opposite sign it was specified that the sum of the heat duties is desired to be 0 with a tolerance of 0.02. The mass flow rate of AMINEIN stream was varied from 50-70 kg/hr to satisfy the desired condition.

4. **Maintaining a approach temperature:** The temperature approach of the cross heat exchangers is also an important pre-requisite for the optimum performance of the process. For this a design specification was defined that regulated the temperature approach by ensuring that the temperature of the outlet stream of HEXLEAN is 10°C above the temperature of the inlet stream to HEXRICH.

For this purpose first the temperature of LEANCOOL and RICHPUMP were defined. It was specified that the temperature of LEANCOOL to be 10^{o}C more than the temperature of RICHPUMP with a tolerance of 0.1. To achieve this we need to vary the AMINEIN mass flow rate from 50-70 kg/hr.

5. **Water balance:** Water balance in the plant has to be maintained in order to have closed loop convergence. For this purpose, the flow rate of the makeup water stream is varied to achieve an overall water balance.

   To ensure water balance we first need to define the mass flow rate of CW, CW1, and MAKEUP WATER, 1, 2 and 3 streams. It was specified that sum of the expression (CW+MAKEUP WATER-CW1-1-2-3) should be equal to zero with a tolerance of 0.02. To attain water balance we need to vary the MAKEUP WATER from 40-60 kg/hr.

CHAPTER-6

RESULTS AND DISCUSSION

After the initial run we found the CO_2 capture to be 75 %. Next sensitivity analyses for the complete process were carried out to see the effect of different parameters on loading and energy required in the form of Reboiler Duty. These were carried out in the Thermodynamic model itself because it is a simplified simulation approach which helps us to get a rough idea about the nature and extent to which the various parameters affect performance. The various sensitivity analyses for the liquid to gas ratio variation in the absorber with lean loading and the variation of reboiler duty due to the effect of L/G ratio , capture percentage , desorber pressure and cross heat exchanger approach were carried out and their results are stated below:

6.1. Effect of Lean Loading on L/G in absorber for 80 % Capture

Results

Table 6-1 Lean Loading vs L/G Data

Lean Loading (mol of CO_2/mol of MEA)	L/G (mol of liquid/mol of gases)
0.12	0.8
0.14	0.86
0.16	0.88
0.18	0.93
0.2	0.99
0.22	1.05
0.24	1.1
0.26	1.2
0.28	1.37
0.3	1.6

Graphical Representation

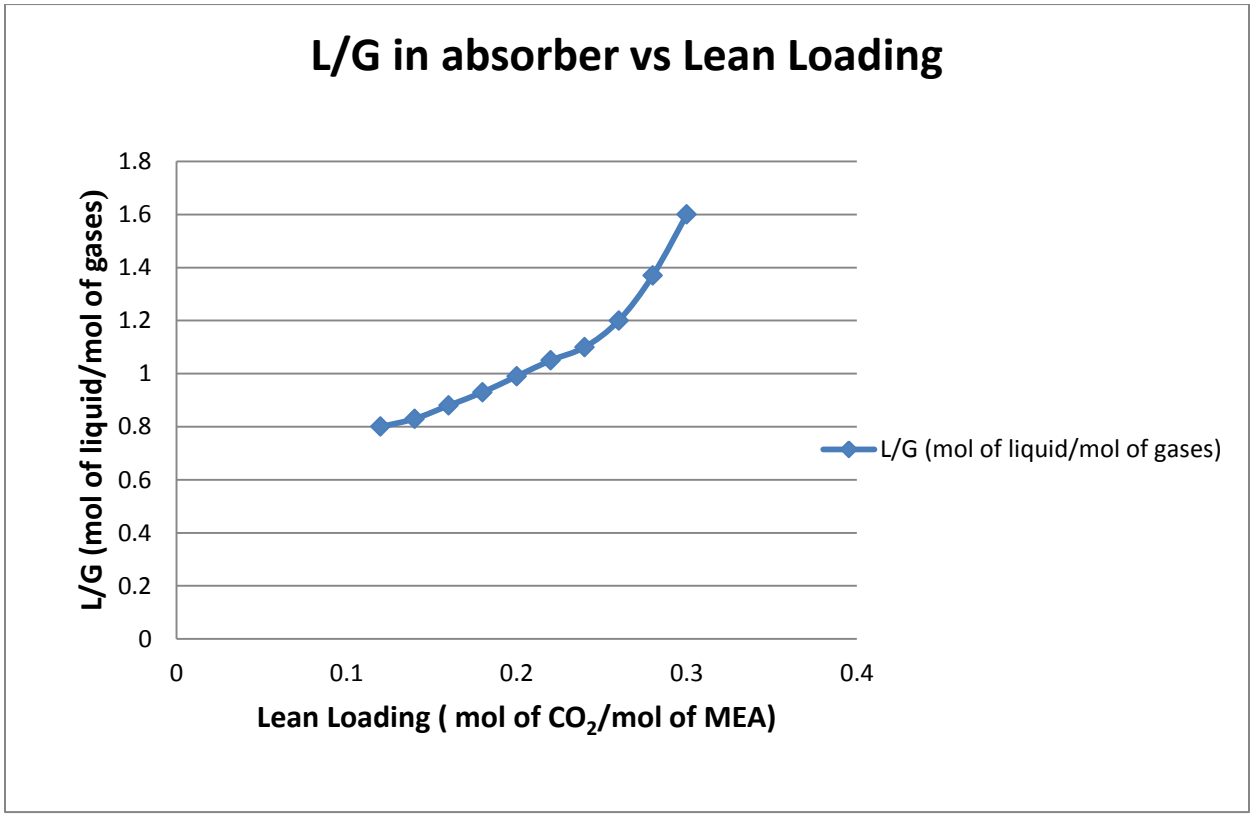

Figure 6-1: Graph representing the change in L/G in absorber with Lean Loading

Discussion

It was seen that the amine flow rate tends to increase with the loading of lean amine stream. This happens because as the loading increases, the capacity to absorb CO_2 decreases. It can also be seen that beyond a certain loading the L/G or amine flow rate required to achieve the required amount of capture increases steeply i.e. a large amount amine is required to sustain 80% capture. Thus the initial loading should be between 0.15-0.25.

6.2. Effect of L/G in Absorber on Reboiler Duty for 80 % Capture

Results

Table 6-2 Data representing variation of Reboiler Duty with L/G in Absorber

L/G (mol total liquid/mol total gas)	Reboiler Duty (kJ/kg CO_2)
0.75	8600
0.8	7000
0.85	6206
0.9	5512
0.95	5350
1	5263
1.2	5115
1.3	5054
1.4	5020
1.5	5004
1.6	5015
1.7	5035
1.8	5078

Graphical Representation

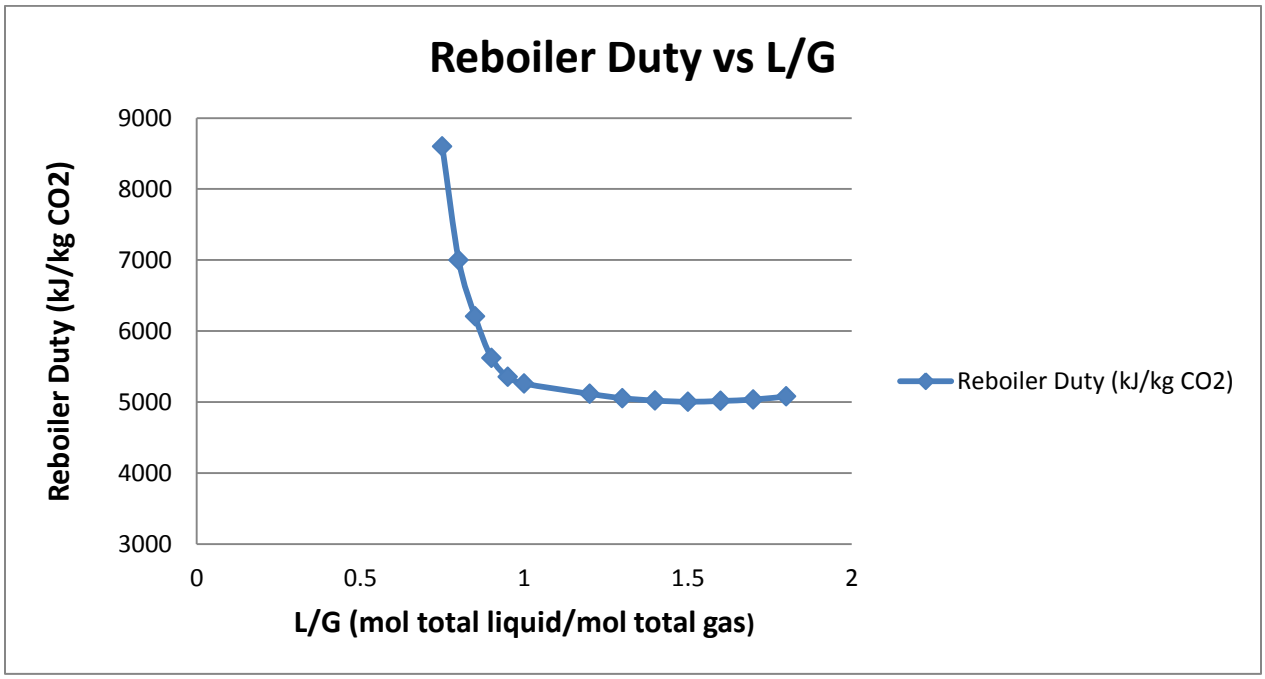

Figure 6-2: Graph representing change in reboiler duty with L/G for 80% capture

Discussion

It can be seen from the above figure that initially at very low loading of lean stream the reboiler duty is very high, because at low loading, the equilibrium partial pressure of CO_2 is very low. As a result a large amount of steam is required to strip the solution to the required lean loading in the desorber and thus a large amount of energy is lost in vaporization and condensation of water. Gradually as the lean loading increases, partial pressure of CO_2 in the amine stream increases as a result of which the amount of steam that is required to facilitate the stripping decreases. So the heat or energy required also decreases thus reducing the reboiler duty. But with increase in loading beyond a limit it again starts increasing because the amount of amine required to achieve 80 % capture also increases.

6.3. Effect of Capture Percentage

Results

Table 6-3 Data representing the different Reboiler duties with respect to changing Lean Loading for different capture percentage

Lean loading (mol of CO_2/ mols of MEA)	Reboiler Duty for 90 % capture (KJ/Kg CO_2)	Reboiler Duty for 85 % capture (KJ/Kg CO_2)	Reboiler Duty for 70 % capture (KJ/Kg CO_2)
0.14	7200	7178	7152
0.16	6440	6295	6263
0.18	5953	5870	5832
0.2	5712	5665	5616
0.22	5690	5618	5561
0.24	5760	5662	5612
0.26	5845	5795	5685
0.28	6016	5912	5760
0.3	6220	6015	5812

Graphical representation

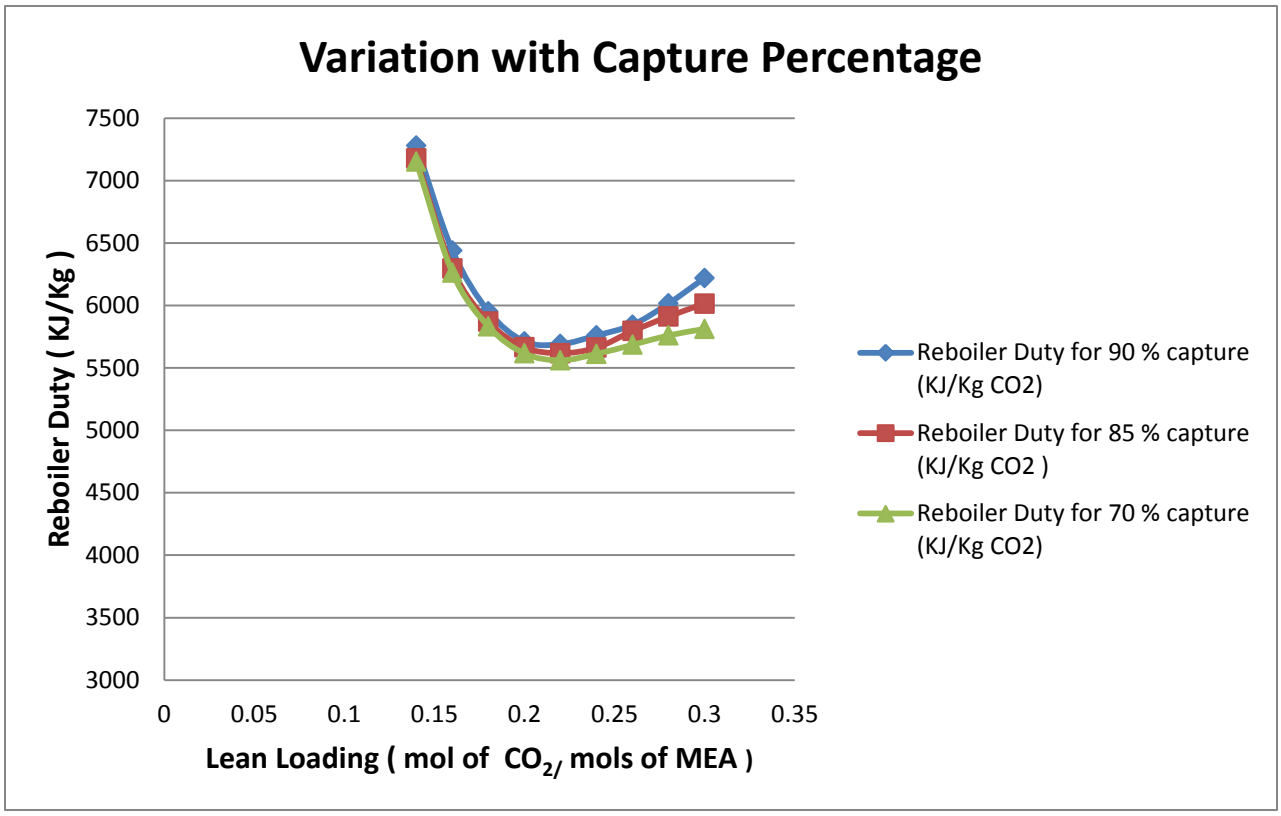

Figure 6-3 Graph showing change in Reboiler Duty with Lean Loading for different capture percentage

Discussion

The main purpose of any sequestration process is to enhance the amount of CO_2 captured. Thus the capture percentage is an important pre-requisite that should be kept in mind. Higher percentage of capture requires more energy and a more efficient process. To verify this the simulation was carried out at 3 different capture percentage – 90 , 85 , 70 and in each case the variation of reboiler duty with lean loading was checked . The results are tabulated above and from the figure 6-3 it can be clearly seen that the reboiler duty increases as we increase the capture percentage. This occurs mainly because to achieve higher capture we need more solvent and more heat which ultimately results in higher reboiler duty.

6.4. Effect of Desorber pressure on Reboiler Duty and Reboiler Temperature for 80 % CO_2 capture.

Results

Table 6-4 Data representing the values of Reboiler Duty and Temperature at different Desorber Pressure

Desorber Pressure (kpa)	Reboiler Duty (KJ/Kg)	Reboiler Temperature (K)
75	7612	370
100	6548	378
125	6020	383
150	5860	387
175	5658	391
200	5510	394
225	5406	396
250	5312	399
275	4250	402
300	4200	405

Graphical Representation

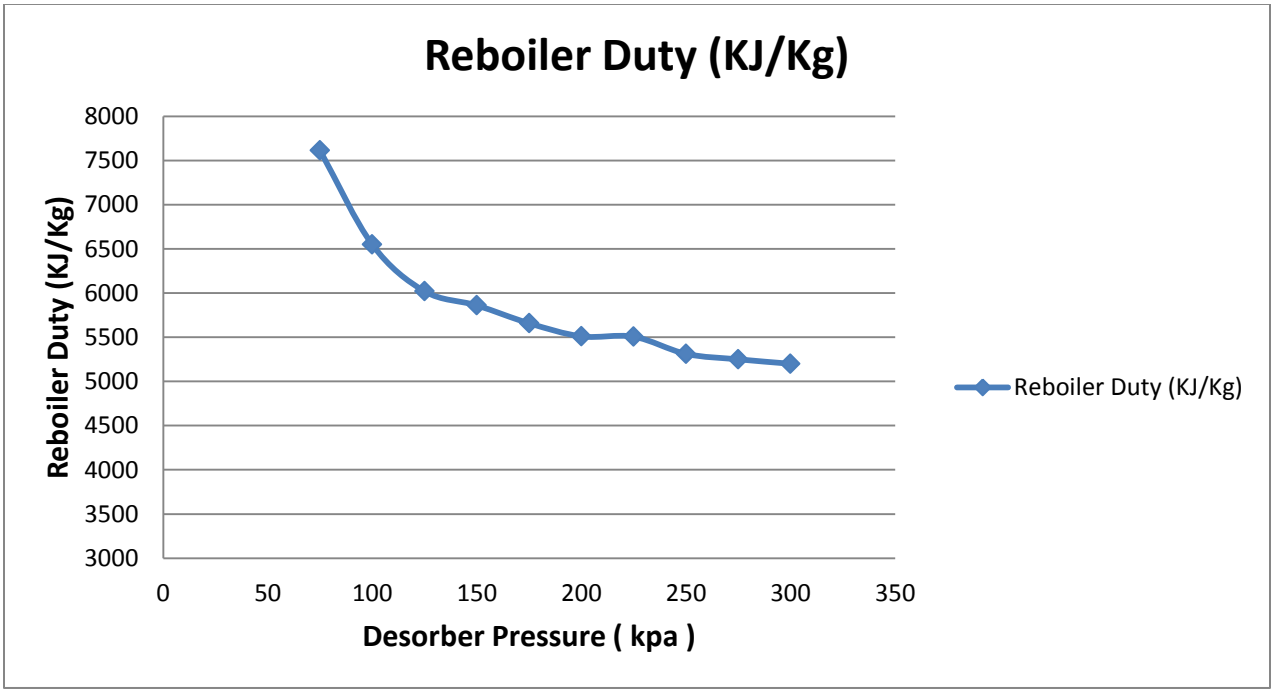

Figure 6-4 Graph showing variation of Reboiler Duty with Desorber Pressure

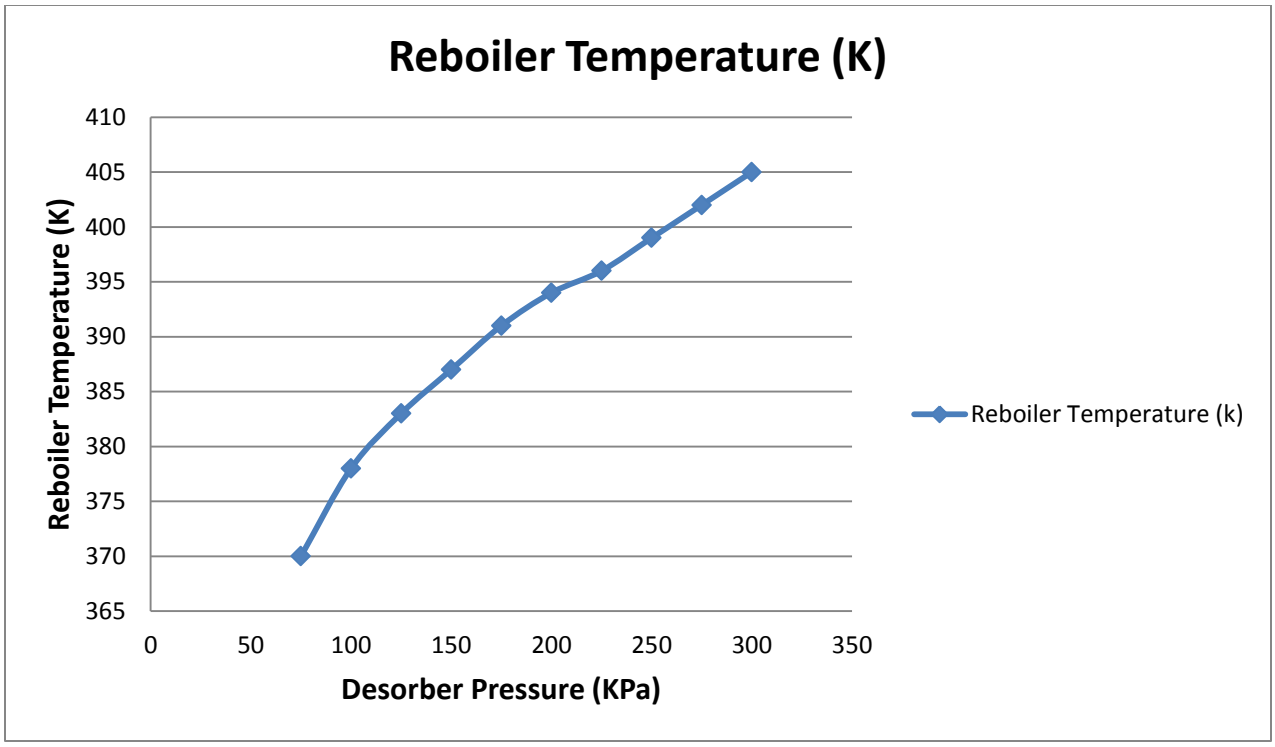

Figure 6-5 Graph Showing Variation of Reboiler Temperature with Desorber Pressure

Discussion

The job of the Desorber mainly is to strip CO_2 from the rich amine and to obtain a lean stream which satisfies required specifications. The reboiler present , has to provide the necessary heat and energy. The pressure in the desorber affects the performance as it changes the temperature. To verify this, data was obtained for the reboiler duty and temperature at different desorber pressure. It can be seen that as the pressure increases the reboiler temperature also increases. This ultimately lessens the burden on the reboiler and less energy is required to strip CO_2. As a result it was found that the reboiler duty decreases gradually with the increasing pressure. But we must be careful as very high pressure can lead to very high temperature which may ultimately degrade the amine solution.

6.5. Effect of approach temperature on the Reboiler Duty for varying Lean Loading

Results :-

Table 6-5 Data representing Reboiler Duties at different Lean Loading for 15°C and 10°C temperature approach

Lean Loading (mol of CO_2 / mol of MEA)	Reboiler Duty For 15 °C Cross Heat Approach(KJ/Kg)	Reboiler Duty 10 °C Cross Heat Approach (KJ/Kg)
0.1	9620	9620
0.12	8112	8112
0.14	7115	7115
0.16	6317	6317
0.18	5933	5889
0.2	5727	5665
0.22	5780	5632
0.24	5801	5653
0.26	5852	5702
0.28	5902	5755
0.3	5965	5806

Graphical Representation

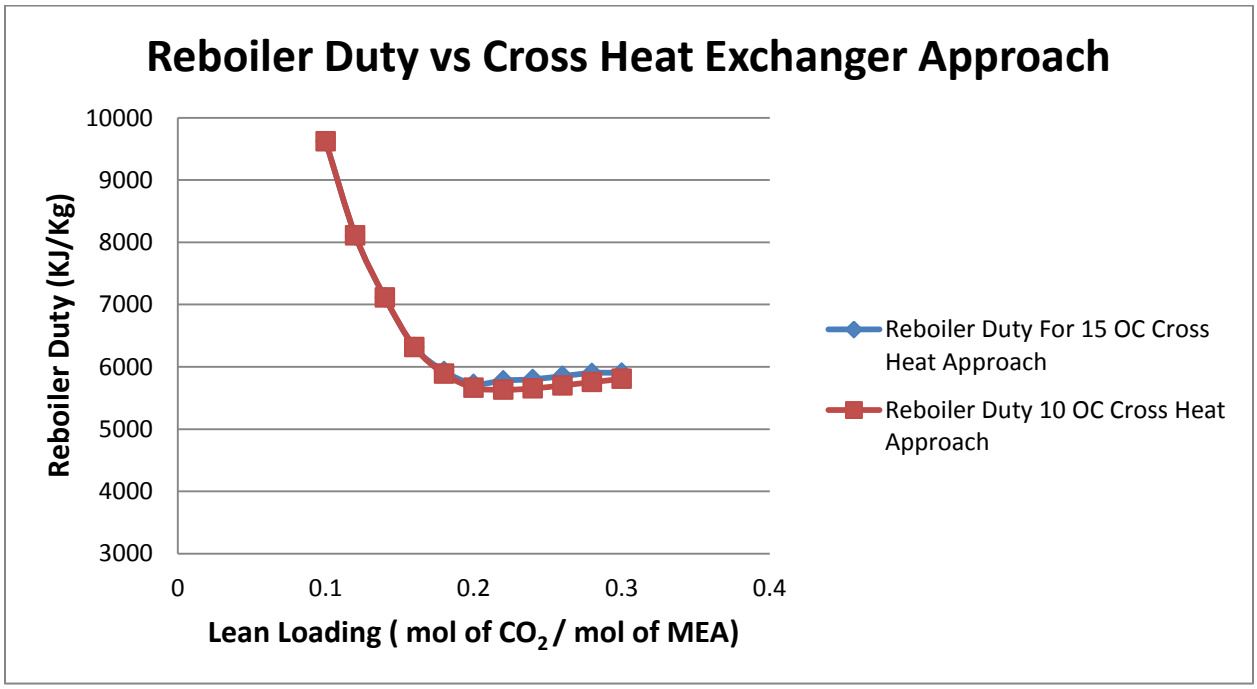

Figure 6-6 Graph Showing Variation of Reboiler Duty due to different Cross heat exchanger approach

Discussion

The heat transfer between the Lean amine and Rich amine takes place through a cross heat exchanger. We need a temperature approach for its proper functioning which also ultimately affects its performance. The initial simulation was carried out using a 10 ^{o}C. When a higher approach is selected it increases the heat requirements of the process. In the above analysis the reboiler duties were generated assuming 10^{o} C and 15^{o} C temperature approach and these data were plotted with respect to varying lean loading. It can be seen that at lower loadings there is no change in the reboiler duty for both the cases. But as we increase the lean loading, the reboiler duty also increases slightly to maintain a higher cross heat exchanger approach..

CHAPTER-7

7.1 CONCLUSION

From the work carried out it can be concluded that the simulation for the CO_2-MEA-H_2O system is a complex process as it as a lot parameters which have to be taken care of. So initially we need to carefully study the actual process and understand the different operations going on. Accordingly the input specifications are to be provided that matches the relevant industrial practices. The thermodynamic model used here is a simplified model which assumes the process to be at equilibrium. The E-NRTL base method selected takes care of the presence of polar ions. The different equilibrium reactions along with the different reaction parameters are also necessary as they represent the mechanism and the components involved in the absorber and desorber. To ensure the convergence of the open-loop flowsheet 5 design specifications have to be incorporated. These also enable us to get a satisfying capture percentage. Later, to get a basic idea about the effect of the parameters like solvent rate, capture percentage, desorber pressure on the Reboiler Duty, Sensitivity analysis were carried out. From the results we could conclude that as the lean loading increases the amount of amine required also increases but the reboiler duty required decreases gradually. Similarly the variations of reboiler duty with capture percentage and cross heat exchanger approach were also studied. The thermodynamic modeling does not give the exact results but provides us the initial knowledge, the required methodology and operation limits and values of different variable which will be used for more complex simulations.

7.2 FUTURE COURSE OF WORK

In simulations carried out using thermodynamic model, the absorber and desorber column were designed to consist of a set of stages, with each stage in equilibrium. The different reactions that take place in the column were also assumed to be at equilibrium. But in reality the reactions are not in equilibrium because mass transfer also takes place and the reaction kinetics, heat transfer rate and mass transfer rate affect the process. Hence, these simulations present the most optimistic results attainable. The main purpose of these simulations is to understand the complete

process and obtain good estimates of the different variables required for converging the system with the more complex rate-based method. These simulations also give us an idea about the effect; the different parameters have on the performance, but are unable to provide us with an optimum value.

Using the input data and the results obtained from a successful equilibrium simulation, one can easily work with a Rate Based Model It incorporates the phenomena of mass transfer , heat transfer , solution kinetics and interface effect as well as the kinetics of chemical reactions and film discretization , which explains the whole process going on . Also using the Rate-Frac Model the dependency of the performance on loading, the packing characteristics, and the column height can be found accurately. Also energy consumption is one of the main constraints of this type of CO_2 capture. So we can work on estimating the total energy requirement of the whole plant and work on optimizing the whole process commercially.

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